

Derivatives of Anthraquinone. 1-Alkyl-
Thio-Ether-5-Sulfonic Acids and
1-5-Dialkyl-Dithio-Ethers

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
COLIN MACKENZIE MACKALL

June, 1920

EASTON, PA.:
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TABLE OF CONTENTS

Acknowledgment	4
Introduction.....	5
Historical.....	5
Outline of Present Investigation.....	6
Materials.....	6
Analytical.....	7
The Compounds Obtained.....	7
I. Anthraquinone-1-alkyl-thio-ether-5-sulfonic acids.....	8
II. Anthraquinone-1-5-dialkyl-dithio-ethers.....	10
III. Anthraquinone-1-5-dialkyl-disulfones.....	12
Biography.....	13

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DERIVATIVES OF ANTHRAQUINONE. 1-ALKYL-THIO-ETHER-5-SULFONIC ACIDS AND 1-5-DIALKYL-DITHIO-ETHERS.¹

Introduction.

The original object in taking up the study of anthraquinone sulfonic acids was to obtain derivatives which could be used for their ready separation and identification. This object was only partially attained but the reaction tried proved interesting and the products obtained appeared worthy of study, so the investigation was shifted from its original purpose and extended in other directions.

On account of the instability of the esters of sulfonic acids the methods used for the identification of carboxy acids² were not promising and our efforts were directed to the replacement of the sulfonic groups.

It was known that the sulfonic acid group of α -anthraquinone sulfonic acids can be replaced by methoxy³ or phenoxy⁴ groups, and that the resulting compounds $C_{14}H_7O_2.OCH_3$ and $C_{14}H_7O_2.OC_6H_5$ are crystalline and have definite, though rather high melting points. Hence it was thought that a compound of the type $C_{14}H_7O_2.SR$ would be of service. *N*-butyl mercaptan was used as being readily available, and it was thought probable that the compound $C_{14}H_7O_2.SC_4H_9$ would have a low melting point, since sulfur compounds usually melt lower than the corresponding oxygen compounds, and since butyl derivatives are apt to melt considerably lower than methyl, and much lower than phenyl. The desired reaction was found to take place readily, although not quantitatively, when the sulfonic acid group is in the α -position. The resulting compounds were found to have convenient melting points suitable for the identification of anthraquinone- α -sulfonic acid, and anthraquinone-1,5- and -1,8-disulfonic acids.

Our study has been extended to the derivatives of other mercaptans.

Historical.

Anthraquinone aliphatic thio-ether sulfonic acids and dithio-ethers may be prepared by the action of aliphatic mercaptans on anthraquinone sulfonic acids in alkaline solution.⁵ In this way Bayer and Company pre-

¹ Revised September 1922.

² *J. Am. Chem. Soc.*, **39**, 124, 304, 701, 1727 (1917); **41**, 75 (1919); **42**, 1043 (1920); and **43**, 629 (1921).

³ Bayer and Co., Ger. pat. 156,762.

⁴ Bayer and Co., Ger. pat. 158,531.

⁵ Bayer and Co., Ger. pat. 224,589.

pared anthraquinone-1-ethyl-thio-ether-5-sodium sulfonate and 1,5-diethyl-thio-ether.

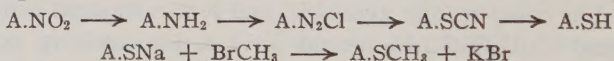
Gattermann⁶ has shown that the nitro group is replaceable by the alkoxy group when treated with sodium alcoholate, thus,



representing the anthraquinone residue by A. He attempted to carry out the analogous reaction with aliphatic mercaptans in order to obtain anthraquinone thio-ethers, but was hindered by the reduction of the nitro group to the amino group. On the other hand, he found that treatment with alkali aromatic mercaptides readily caused a quantitative replacement of the nitro group with the formation of aromatic thio-ethers.



Gattermann⁷ has also prepared anthraquinone aliphatic thio-ethers and thio-ether sulfonic acids indirectly by diazotizing amino-anthraquinones, or amino-anthraquinone sulfonic acids in conc. sulfuric acid. Subsequent treatment of the diazo compound with potassium thiocyanate yielded anthraquinone thiocyanate which on boiling with alcoholic potash gave the mercaptan, which with alkyl halide yielded the thio-ether or thio-ether sulfonic acid. In this way he prepared anthraquinone- α -methyl-thio-ether; anthraquinone- α -ethyl-thio-ether; anthraquinone-1-methyl-thio-ether-5-potassium sulfonate; and anthraquinone-1-methyl-thio-ether-8-potassium sulfonate, thus,



Outline of Present Investigation.

We have found that anthraquinone-1-5-disulfonic acid, on heating with alkyl mercaptans in alkaline solution, reacts readily to form anthraquinone-1-5-thio-ether-sulfonic acids and 1-5-dialkyl-dithio-ethers, the sulfonic groups being replaced in turn.

Materials

The anthraquinone-1-5-disodium sulfonate was obtained through the courtesy of E. I. du Pont de Nemours and Company. The methyl mercaptan was generated as required by dropping dimethyl sulfate into warm sodium hydrosulfide, which was prepared by warming crystallized sodium sulfide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, to about 90° and saturating with hydrogen sulfide. The ethyl mercaptan was prepared in a similar manner using sodium ethyl sulfate. The propyl, butyl and *iso*-amyl mercaptans were prepared by the catalytic method of Kramer and Reid.⁸

⁶ Bayer and Co., Ger. pat. 75,054.

⁷ *Ann.*, **393**, 113 (1912).

⁸ Kramer and Reid, *J. Am. Chem. Soc.*, **43**, 880 (1921).

Analytical.

1. **Water of Hydration.**—One-g. samples were exposed to an atmosphere of 50% humidity⁹ for 48 hours, then heated to constant weight in a vacuum at 110°, 2 to 4 hours being generally sufficient to remove all the water. Analyses for sulfur and metals were made on the dry samples.

2. **Sulfur.**—Sulfur was determined by means of the Parr bomb,¹⁰ using a 0.2 g. sample and 5 g. of sodium peroxide, with subsequent precipitation of barium sulfate.

3. **Sodium, Barium, Strontium, Calcium.**—One-half g. samples were ignited in a platinum crucible until the carbon was burned off as completely as possible. The residue was then evaporated with conc. sulfuric acid, and re-ignited with ammonium carbonate to constant weight. The metal was weighed as the sulfate.

The Compounds Obtained.

The anthraquinone-thio-ether sodium sulfonates are moderately soluble in water, the derivatives of the lower mercaptans being more soluble than those of the higher mercaptans. They crystallize from water in orange or orange-red needles containing one molecule of water of hydration. Salts of other bases are highly colored, ranging from yellow through through shades of orange to red and are mostly well crystallized.

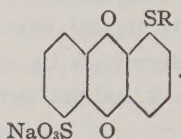
The anthraquinone dithio-ethers are insoluble in water, slightly soluble in alcohol and soluble in benzene, the solubility in benzene increasing with the size of the alkyl group. When crystallized from benzene they form lustrous crystals varying in color from light yellow to red.

The corresponding sulfones are high melting, slightly yellow crystalline powders.

⁹ A dead air humidor containing 44% H_2SO_4 was used to obtain this humidity.

¹⁰ Parr, *J. Ind. Eng. Chem.*, **11**, 230 (1919).

I. Anthraquinone-1-alkyl-thio-ether-5-sulfonic Acid.



1. Methyl or ethyl mercaptans were passed through a wide tube at the rate of one bubble per second into an alkaline suspension of anthraquinone-1-5-disodium sulfonate. The mixture was gently boiled and vigorously stirred until the separation of yellow or orange crystals of anthraquinone-thio-ether-sodium sulfonate indicated that the reaction was complete. The reaction must be interrupted at the proper moment to prevent the formation of large amounts of the dithio-ether by the replacement of the second sulfonic acid group by the thio-alkyl group. The product was cooled, filtered, washed with a little water, dried and extracted with benzene to remove the dithio-ether which was always formed in small amounts. The crude anthraquinone-thio-ether-sodium sulfonates were recrystallized from water.

2. Anthraquinone-propyl-, butyl-, and iso-amyl-thio-ether-sulfonic acids were prepared by refluxing an alkaline suspension of anthraquinone-1-5-disodium sulfonate with slightly more than the calculated amount of mercaptan. The products were purified as under I, 1 above.

PREPARATION OF ANTHRAQUINONE-1-ALKYL-THIO-ETHER-5-SODIUM SULFONATES.
 $1,5\text{-RS.C}_{14}\text{H}_6\text{O}_2.\text{SO}_3\text{Na.H}_2\text{O}.$

Alkyl.	Sulfonate. G.	Water. Cc.	NaOH. G.	RSH.	Time. Hrs.	Yield. G.	%.
Methyl	50	400	13	gas	2	30	65
Ethyl	100	600	26	gas	1	38	42
Propyl	50	1000	10	12	1	23	50
Butyl	50	500	16	15	7	30	62
iso-Amyl	100	1000	32	34	15	55	55

ANALYSES AND PROPERTIES OF SODIUM SALTS. $1,5\text{-RS.C}_{14}\text{H}_6\text{O}_2.\text{SO}_3\text{Na.H}_2\text{O}.$

Alkyl.	Water.		Sodium.		Color and form.
	Calc. %.	Found. %.	Calc. %.	Found. %.	
Methyl	4.81	4.86	6.46	6.27	orange-red needles
Ethyl	4.64	4.93	6.21	6.04	dark orange-red needles
Propyl	4.48	4.42	5.98	5.92	rich orange-red needles
Butyl	4.33	4.41	5.77	5.77	orange-red needles
iso-Amyl	4.19	4.26	5.58	5.43	orange-red needles

Barium, Calcium and Strontium Salts.—These were made by dissolving the sodium salts in hot water and adding the calculated amounts of the chlorides of the other metals. The resulting salts are extremely insoluble and are purified by boiling out with water.

BARIUM SALTS. 1,5-(RS.C₁₄H₆O₂SO₃)₂Ba.

Alkyl.	Barium.		Color and form.
	Calc. %.	Found. %.	
Methyl	17.09	17.00	red needles
Ethyl	16.51	16.50	red crystal powder
Propyl	15.97	15.58	orange-red needles
Butyl	15.47	15.43	red crystals
<i>iso</i> -Amyl	14.99	14.56	red crystals

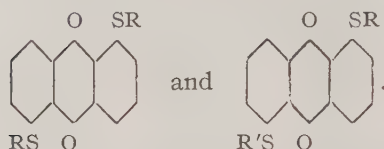
The strontium and calcium salts also were made of the butyl acid, the strontium salt being anhydrous, (Sr, calc. 10.45; found, 10.40). The calcium salt, unlike the others contains 4 molecules of water of crystallization, showing by analysis 8.12% of water and 5.09% of calcium compared to 8.35 and 5.07% respectively, by formula. The barium salt is a deep red and the calcium salt an orange-red, while the strontium salt is intermediate.

Aniline, o- and p-Toluidine Salts.—These salts were made by adding the corresponding hydrochlorides to the hot, saturated solutions of the sodium salts. All of them are very insoluble and precipitate. They were purified by extraction with hot water. They all separate as fine yellow needles which melt with decomposition at from 250° to 300°. These temperatures are not sharp enough for characterization as had been hoped. The *o*-toluidine salts decompose at lower temperatures than the aniline or *p*-toluidine.

ANILINE, *o*-TOLUIDINE AND *p*-TOLUIDINE SALTS. 1,5-RS.C₁₄H₆O₂.SO₃H₃NAr.

Alkyl.	Base.	Decomp. temp. ° C.	Sulfur.	
			Calc. %.	Found. %.
Methyl	Aniline	290-299	15.00	14.70
	<i>o</i> -Toluidine	285-290	14.53	14.75
	<i>p</i> -Toluidine	298-304	14.53	14.50
Ethyl	Aniline	276-285	14.53	14.30
	<i>o</i> -Toluidine	264-274	14.08	14.10
	<i>p</i> -Toluidine	276-285	14.08	14.25
Propyl	Aniline	270-277	14.08	14.15
	<i>o</i> -Toluidine	255-257	13.66	13.75
	<i>p</i> -Toluidine	268-275	13.66	13.85
Butyl	Aniline	257-259	13.66	13.80
	<i>o</i> -Toluidine	234-237	13.26	13.35
	<i>p</i> -Toluidine	256-260	13.26	13.10
<i>iso</i> -Amyl	Aniline	263-265	13.26	13.10
	<i>o</i> -Toluidine	250-254	12.89	12.80
	<i>p</i> -Toluidine	267-277	12.89	12.90

II. 1,5-Anthraquinone Dialkyl Dithio-ethers.



When the two alkyl groups are the same, these may be obtained directly by heating the sodium 1,5-disulfonate with excess of alkali and mercaptan for a long time. They are always formed to a greater or less extent in the preparation of the intermediate thio-ether sulfonates described above and are obtained by extraction of the crude products with benzene. The diethyl and dibutyl compounds were obtained in this way.

The intermediate monosulfonate may be isolated and purified and the second alkyl group, which may be the same as the first or different, introduced. Of course the mixed thio-ethers must be prepared in this way.

The alkyl thio-ether sodium sulfonate is suspended in water, containing an excess of caustic soda with the mercaptan, and the mixture boiled. The reaction is slow on account of the low solubility of the sodium salts, particularly of those containing the higher alkyl groups. It is best to introduce the lower alkyl group first. The resulting dithio-ethers are extracted with hot benzene and recrystallized from benzene, or alcohol, or mixtures of the two. The details of the various preparations are given in tabular form.

PREPARATION OF 1,5-ANTHRAQUINONE DIALKYL DITHIO-ETHERS.

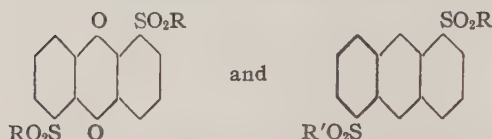
First alkyl.	Alkyl introduced.	Wt. sulfonate. G.	Vol. water. Cc.	Caustic soda. G.	Wt. RSH. G.	Time. Hours.	Yield. G.
Methyl	Methyl	5	500	2	gas	4	4
	Ethyl	10	500	4	gas	4	1
	Propyl	8	500	2	6	23	5
	Butyl	8	500	2	4.6	22	5
	<i>iso</i> -Amyl	8	500	2	4.4	6	6
Ethyl	Propyl	5	350	2	5	30	4
	Butyl	5	350	2	5	30	4
	<i>iso</i> -Amyl	5	300	2	5	12	4.5
Propyl	Propyl	10	750	2	6	20	7
	Butyl	8	750	2	6	7	3
<i>iso</i> -Amyl	Butyl	10	1000	2	5	41	6.5
	<i>iso</i> -Amyl	10	300	2	5	11	2.5

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DITHIO-ETHERS. 1,5-
 $C_{14}H_6O_2(SR)_2$ AND 1,5-RS. $C_{14}H_6O_2$.SR'.

Alkyls.		M. p. °C.	Sulfur.		Color and form.
			Calc. %.	Found. %.	
Methyl	Methyl	Chars.	21.35	21.03	red needles
	Ethyl	229	20.40	20.35	yellow needles
	Propyl	209	19.53	19.45	orange needles
	Butyl	173.5	18.73	18.50	yellow needles
	<i>iso</i> -Amyl	175	17.99	17.90	orange-yel. leaflets
Ethyl	Ethyl	226.5	19.53	19.40	orange grains
	Propyl	188.5	18.73	18.65	orange grains
	Butyl	156	17.99	17.75	red crystals
	<i>iso</i> -Amyl	152	17.31	17.25	gold-yellow plates
Propyl	Propyl	227	17.99	18.30	orange cryst. powder
	Butyl	175	17.31	16.95	orange prisms
Butyl	Butyl	159.5	16.68	16.65	yellow needles
	<i>iso</i> -Amyl	134	16.09	15.80	orange needles
<i>iso</i> -Amyl	<i>iso</i> -Amyl	158.5	15.55	15.59	yellow needles

Comparing these, we see that the dimethyl compound has the highest melting point and that the melting point is progressively lowered as heavier alkyl groups are substituted for one of the methyls. Gattermann gives the diethyl thio-ether as melting at 230°.

III. 1,5-Anthraquinone Dialkyl Disulfones.



These were prepared by oxidizing the dithio-ethers with fuming nitric acid. They separate as faintly yellow crystalline powders, when their nitric acid solutions are poured into hot water. They are very slightly soluble in most solvents.

PROPERTIES AND ANALYSES OF 1,5-ANTHRAQUINONE DIALKYL DISULFONES, 1,5- $\text{C}_{14}\text{H}_6\text{O}_2$ - $(\text{SO}_2\text{R})_2$ AND 1,5- $\text{R}'\text{SO}_2\cdot\text{C}_{14}\text{H}_6\text{O}_2\cdot\text{SO}_2\text{R}$.

Alkyls.		M. p. °C.	Sulfur.		Form.
			Calc. %.	Found. %.	
Methyl	Methyl	chars.	17.60	17.53	powder
	Ethyl	> 300	16.95	16.90	fine needles
	Propyl	291	16.34	16.50	crystalline grains
	Butyl	264	15.78	15.75	crystalline grains
	<i>iso</i> -Amyl	266	15.25	15.00	crystalline grains
Ethyl	Ethyl	269.5	16.34	16.40	fine needles
	Propyl	243.5	15.78	15.65	fine needles
	Butyl	194	15.25	15.45	powder
	<i>iso</i> -Amyl	198	14.76	14.80	powder
Propyl	Propyl	265	15.25	15.15	fine needles
	Butyl	220	14.76	14.95	crystalline grains
Butyl	Butyl	184.5	14.30	14.10	crystalline powder
	<i>iso</i> -Amyl	203.5	13.87	14.00	crystalline powder
<i>iso</i> -Amyl	<i>iso</i> -Amyl	202	13.46	13.50	powder

BIOGRAPHY

Colin Mackenzie Mackall was born at Baltimore, Maryland on December 26, 1884. He received his primary education in the public schools of that city, and graduated from the Baltimore City College in 1904. He then entered the University of Virginia, from which Institution he received the degrees of Bachelor of Arts in 1909 and Bachelor of Science in Chemistry in 1910. The following year he was Assistant Chemist in the Bureau of Chemistry, U. S. Department of Agriculture, and in attendance upon courses at George Washington University. Upon the completion of a thesis in absentia, this University conferred the degree of Master of Science upon him in 1913.

From 1911 to 1916 he was Professor of Chemistry in the University of the South, Sewanee, Tennessee. Resigning his position in order to continue his studies, he entered the Johns Hopkins University in the Fall of 1916 taking Chemistry, Physical Chemistry and Mineralogy.

He entered the Officers' Training Camp in the Summer of 1917, and was commissioned Captain, Coast Artillery Corps, and went overseas. He was transferred to the Chemical Warfare Service, and served as Gas Officer of the Second Division, Assistant Gas Officer of the First Corps, and Assistant Chief, and later Chief, of Chemical Warfare Service, Second Army. He was promoted to Major C. W. S. in September 1918.

After the armistice he attended the University of Paris for one semester, and re-entered the Johns Hopkins University as a University Fellow in the Fall of 1919.

